

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office. © Copyright, 1968, by the American Chemical Society

VOLUME 90, NUMBER 26

DECEMBER 27, 1968

Physical and Inorganic Chemistry

γ Radiolysis of Ethanol Vapor¹

K. M. Bansal² and G. R. Freeman

Contribution from the Department of Chemistry, University of Alberta,
Edmonton, Alberta, Canada. Received August 1, 1968

Abstract: The product yields changed only slightly as the temperature was increased from 60 to 200°. Increasing the ethanol pressure from 45 to 1700 torr at 150° decreased the yields of hydrogen, acetaldehyde, and ethylene but had no effect on those of methane and carbon monoxide. The changes of yield with pressure were interpreted in terms of excited molecules whose decomposition lifetimes had lower limits of 1.9×10^{-10} and 3.0×10^{-10} sec. The hydrogen and acetaldehyde yields decreased with increasing dose; this was attributed to the scavenging of electrons by acetaldehyde, with the ultimate formation of $(\text{CH}_3\text{CHO}^-) \cdot n\text{C}_2\text{H}_5\text{OH}$. Propylene scavenges hydrogen atoms and other free radicals, but not ions or electrons in this system. The efficiency of scavenging methyl radicals increases with increasing pressure. Sulfur hexafluoride scavenges electrons; some of the resultant intermediates or products cause the yields of acetaldehyde and diethyl ether to increase. Direct formation of molecular hydrogen from ion-electron neutralization in ethanol vapor at 150° is negligible. Ammonia has no effect on the rates of formation of the ethanol radiolysis products because neutralization of either $(\text{C}_2\text{H}_5\text{OH})_m\text{H}^+$ or $(\text{C}_2\text{H}_5\text{OH})_m\text{NH}_4^+$ by an electron results in the formation of a hydrogen atom, and the ultimate products are the same.

The present study of the radiolysis of ethanol vapor was undertaken with a view to obtain more information about the reaction mechanism. The effects of temperature, pressure, and dose, and of the additives propylene (free-radical scavenger), sulfur hexafluoride (electron scavenger), and ammonia (proton scavenger) on the product yields were measured.

Very few studies of the radiolytic decomposition of ethanol vapor have been made so far.³⁻⁷ The reported results are incomplete and are sometimes in conflict with each other.

Hotta, *et al.*,⁸ have studied the addition of ethanol to ethylene, induced by γ radiolysis in the gas phase at 175°.

(1) This work received financial assistance from the National Research Council of Canada.

(2) Holder of National Research Council of Canada Studentship and University of Alberta Graduate Fellowship.

(3) J. M. Ramaradhya and G. R. Freeman, *Can. J. Chem.*, **39**, 1836 (1961).

(4) J. M. Ramaradhya and G. R. Freeman, *ibid.*, **39**, 1843 (1961).

(5) J. J. Myron and G. R. Freeman, *ibid.*, **43**, 1484 (1965).

(6) L. W. Sieck and R. H. Johnsen, *J. Phys. Chem.*, **69**, 1699 (1965).

(7) A. R. Anderson and J. A. Winter in "The Chemistry of Ionization and Excitation," G. R. A. Johnson and G. Scholes, Ed., Taylor & Francis Ltd., London, 1967, p 197.

(8) H. Hotta, H. Kurihara, and T. Abe, *Bull. Chem. Soc. Japan*, **40**, 714 (1967).

Experimental Section

Materials. Benzene-free absolute ethanol from Reliance Chemical Co. was purified as described earlier.⁹

Sulfur hexafluoride (Matheson Co.), ammonia (Canadian Industries Ltd.), and propylene (Phillips Research Grade) were degassed by trap-to-trap distillation and stored under vacuum in Pyrex vessels.

Sample Handling. Spherical Pyrex irradiation cells of 500 ml volume were cleaned, evacuated, and baked for 3 hr at 500° before filling.

Materials to be distilled into the irradiation cells were measured in the vacuum line as liquids at a low measured temperature in a calibrated tube, or as gases in standard volumes at 25°.

The filled and sealed irradiation cells were placed in an electric furnace, heated to the desired temperature, and irradiated in a Gammacell 220 (Atomic Energy of Canada Ltd.). Unless otherwise stated, the samples were irradiated at $150 \pm 2^\circ$.

The dose rate was 4×10^{19} eV/(g hr), measured with ethylene and assuming $G(\text{H}_2) = 1.31$, which is the average of the values of Back^{10a} and Holtslander.^{10b,c} Sufficient ethylene was placed in the cell so that the electron density of ethylene in the dosimeter was approximately the same as that of ethanol in the ethanol samples.

(9) J. C. Russell and G. R. Freeman, *J. Phys. Chem.*, **71**, 755 (1967).

(10) (a) R. A. Back, T. W. Woodward, and K. A. McLaughlan, *Can. J. Chem.*, **40**, 1380 (1962); (b) W. J. Holtslander and G. R. Freeman, *ibid.*, **45**, 1649 (1967); (c) W. J. Holtslander, Ph.D. Thesis, University of Alberta, 1966.

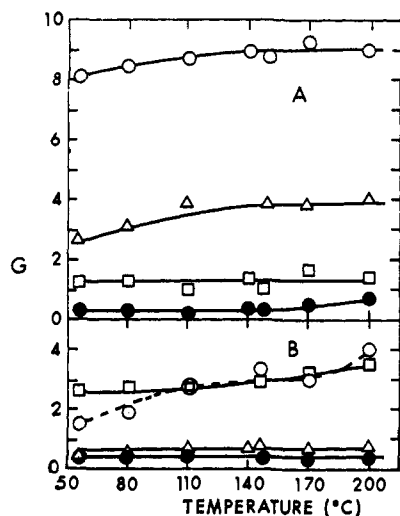


Figure 1. Product yields as a function of temperature in the radiolysis of ethanol vapor (0.66 g/l.): (A) \circ , hydrogen; Δ , acetaldehyde; \square , ethylene; \bullet , ethane; (B) \square , 2,3-butanediol; \circ , methane; Δ , carbon monoxide; \bullet , 1,2-propanediol.

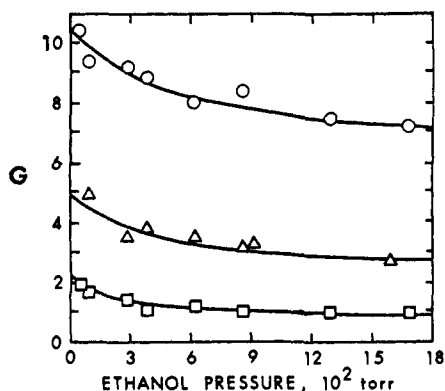


Figure 2. Product yields from ethanol radiolysis as a function of pressure (temperature, 150°): \circ , hydrogen; Δ , acetaldehyde; \square , ethylene. The points represent experimental results; the solid lines were calculated from equations in the text.

The dose rate in ethanol was calculated from the dose rate in ethylene by using the Bethe equation.¹¹

The radiolysis products were analyzed by gas chromatography. Authentic samples of all the identified products were used to determine the calibration factors. A preliminary analysis of the gaseous products was made by low-temperature distillation in a vacuum line and measurement in a McLeod-Toepler apparatus.

Results

Effect of Temperature at Constant Density. Samples were irradiated to a dose of 1.2×10^{20} eV/g at temperatures in the range 60–200°.

Results obtained for an ethanol density of 0.66 g/l. are shown in Figure 1. The hydrogen and acetaldehyde yields each increased by about one unit as the temperature was increased from 60 to about 140°, then remained constant up to 200°. The methane yield tended to behave in the same way, but began to increase again at temperatures above about 170°. The yield of 2,3-butanediol gradually increased by 0.9 unit over the temperature range from 60 to 200°. The G values of ethylene (1.3), carbon monoxide (0.7), and 1,2-propanediol (0.4) were independent of temperature. That

(11) G. J. Hine and G. L. Brownell, "Radiation Dosimetry," Academic Press, New York, N. Y., 1956, p 98.

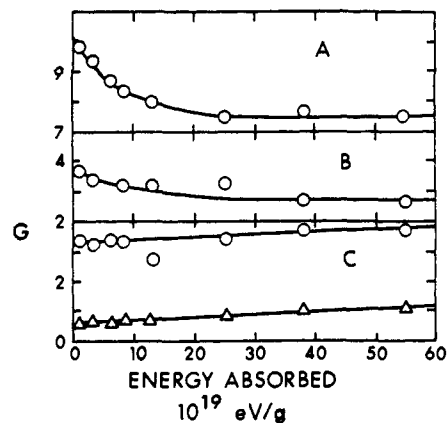


Figure 3. Product yields from ethanol radiolysis as a function of dose (ethanol pressure, 860 torr; temperature, 150°): (A) hydrogen; (B) acetaldehyde; (C) \circ , methane; Δ , carbon monoxide.

of ethane (0.3) was independent of temperature up to 150°, above which the yield began to increase slightly.

The gaseous product yields from ethanol at a density of 0.16 g/l. were also measured at temperatures from 60 to 200°. The variations in the yields with temperature were similar to those at the higher density.

Effect of Ethanol Pressure at 150°. The ethanol pressure was varied from 45 to 1700 torr (0.078–2.96 g/l.). The samples were irradiated to a dose of 8×10^{19} eV/g.

As the pressure increased the yields of hydrogen, acetaldehyde, and ethylene decreased as shown in Figure 2. The yields of methane (3.3), ethane (0.3), and carbon monoxide (0.7) were independent of pressure. Those of 2,3-butanediol (3.1) and 1,2-propanediol (0.4) were too scattered to indicate whether they were pressure dependent or not.

Effect of Dose at 150°. The dose was varied from 1.0×10^{19} to 5.5×10^{20} eV/g in ethanol at a pressure of 860 torr (1.50 g/l.). The hydrogen yield decreased from 9.8 at 1.0×10^{19} eV/g to 7.4 at 2.5×10^{20} eV/g, then remained constant as the dose was increased further (Figure 3A). The acetaldehyde yield behaved similarly, but the decrease was only from 3.6 to 2.6 (Figure 3B). The yields of methane and carbon monoxide increased gently over the entire dose range (Figure 3C). The G values of ethylene (1.1), ethane (0.3), and diethyl ether (0.15) were independent of dose. Because of experimental difficulties the yields of 2,3-butanediol, 1,2-propanediol, and acetylene were only measured over the range 8×10^{19} – 5.5×10^{20} eV/g, over which range the yields were constant.

In Table I, the first two columns of numbers indicate the yields of products at different doses at 150° (860 torr), the third column indicates the effect of decreasing the pressure, and the fourth indicates that of decreasing the temperature.

Effects of Additives at 150°. Propylene, ammonia, and sulfur hexafluoride were added to the ethanol. The dose used was 8×10^{19} eV/g.

The product yields from the mixtures are reported as g values

$$g(P) = \frac{G(P)_{\text{obsd}} - G(P)_{\text{ad}} \epsilon_{\text{ad}}}{\epsilon_{\text{C}_2\text{H}_5\text{OH}}} \quad (i)$$

where $G(P)_{\text{obsd}}$ is the observed yield of P from the mix-

Table I. Comparison of the Reported Yields of the Various Products from the Radiolysis of Ethanol Vapor

Product	Present work				G (product)					
					Ref 3	Ref 5	Ref 6	Ref 7	Ref 8	
Hydrogen	9.9	8.4	10.0	9.9	7.6 (9.2)	7.5	10.8	9.2	10.3	
Methane	3.3	3.3	3.3	1.2	1.7 (2.4)	2.3	0.9	0.3	4.6	
Carbon monoxide	0.6	0.7	0.7	0.7	1.1 (0.9)	0.6	1.2			
Ethane	0.3	0.3	0.3	0.3	0.2 (0.2)	0.2	0.65			
Ethylene	1.1	1.1	1.6	1.3	0.7 (1.4)	1.2	1.6			
Acetylene		0.26			0.03	0.09	0.30			
Formaldehyde		0.8			0.9		0.9			
Acetaldehyde	3.6	3.2	4.8		4.5	3.5	4.2			
Diethyl ether	0.15	0.15					0.07			
1,2-Propanediol		0.4	0.4		0.15	0.9	0.16			
2,3-Butanediol		3.1			1.2	3.1	1.2			

	Radiation									
	γ	γ	γ	γ	α	γ	2 MeV e ⁻	γ	γ	
Dose, 10 ²⁰ eV/g	0.1	0.8	0.8	1.3	6 (0.05)	4	~0.7	2	0.3	
Dose rate, 10 ¹⁹ eV/(g hr)	4	4	4	4	1	6	~100	2	0.6	
G(dosimeter)	C ₂ H ₄ → H ₂				Fricke	C ₂ H ₄ → H ₂ (-C ₂ H ₂)		N ₂ O → N ₂	Fricke	
	1.31				5.5	1.28	71.9	10.6		
Temp, °C	150	150	150	60	108	105	25	108	175	
Pressure, torr	860	860	92	72	660	800	45	760	3040	
Volume, ml	500	500	500	500	1000	500	2040	130	50	

ture, $G(P)_{ad}$ is the yield of P from pure additive, and ϵ_{ad} and $\epsilon_{C_2H_5OH}$ are the electron fractions of additive and ethanol, respectively.

1. Hydrogen Yield. At 850 torr of ethanol, propylene reduced $g(H_2)$ from 8.4 to 1.5, whereas at 92 torr of ethanol the reduction was from 9.9 to 2.5 (Figure 4). About 25 mol % of propylene was required to cause the maximum amount of reduction. The values of $g(H_2)$ were calculated using $G(H_2)_{C_3H_6}$ values taken from the curve in Figure 5 at the appropriate total pressure.

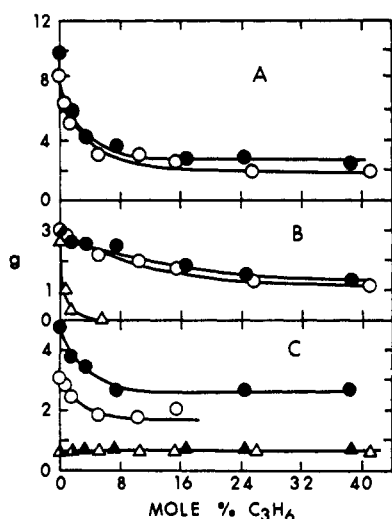


Figure 4. Product yields from ethanol-propylene mixtures (temperature, 150°; ethanol pressure: open points, 860 torr; filled points, 92 torr): (A) hydrogen; (B) ○, ●, methane; △, ▲, 2,3-butanediol; (C) ○, ●, acetaldehyde; △, ▲, carbon monoxide.

Both portions of the hydrogen yield from ethanol, that scavengable and that not scavengable by propylene, increase with decreasing pressure, as does $G(H_2)$ from propylene itself.

Sulfur hexafluoride added to 860 torr of ethanol decreased $g(H_2)$ from 8.4 to 5.4 (Figure 6). Less than 0.2 mol % of sulfur hexafluoride was required to cause the maximum reduction.

The addition of 5.2 mol % of propylene and 3.2 mol % of sulfur hexafluoride to 860 torr of ethanol reduced $g(H_2)$ to 2.7, which is lower than that caused by the separate addition these amounts of propylene ($g \approx 3.3$) or sulfur hexafluoride ($g \approx 5.3$).

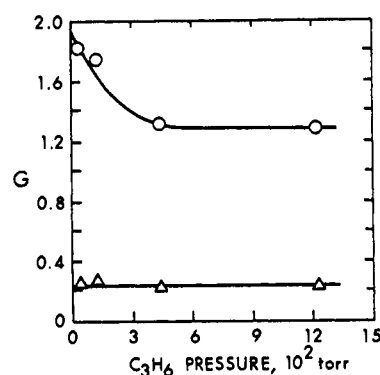


Figure 5. $G(H_2)$ and $G(CH_4)$ from pure propylene as a function of pressure (temperature, 150°): ○, hydrogen; △, methane.

Up to 7 mol % of ammonia had no effect on the hydrogen yield. In calculating $g(H_2)$, $G(H_2)_{NH_3} = 10.0^{12}$ was used.

2. Methane Yield. At 850 torr of ethanol, propylene decreased $G(CH_4)$ from 3.3 to 1.2, and at 92 torr of ethanol the reduction was from 3.3 to 1.5 (Figure 4). The values of $g(CH_4)$ were calculated using $G(CH_4)_{C_3H_6} = 0.24$, at all pressures (Figure 5).

Thus both the scavengable and unscavengable portions of the methane yield are essentially independent of pressure in the range studied, as is $G(CH_4)$ from propylene itself.

Neither sulfur hexafluoride (Figure 6) nor ammonia affected the methane yield.

3. Carbon Monoxide Yield. $g(CO)$ was unaffected by propylene (Figure 4), sulfur hexafluoride, or ammonia.

4. Yields of Other Products. Because of analytical difficulties, all the remaining ethanol products were not

(12) F. T. Jones and T. J. Sworski, *Trans. Faraday Soc.*, **63**, 2411 (1967).

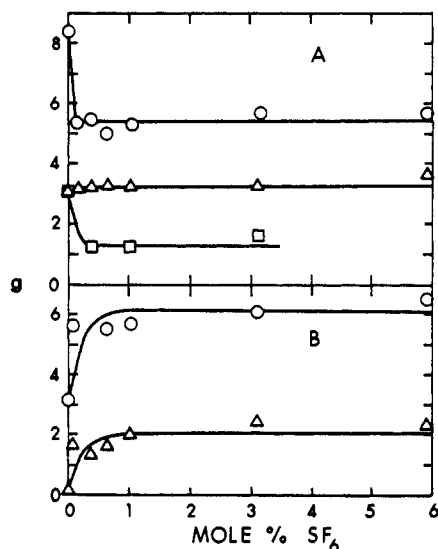


Figure 6. Product yields in the radiolysis of ethanol-sulfur hexafluoride mixtures (temperature, 150°; ethanol pressure, 860 torr): (A) O, hydrogen; Δ, methane; □, 2,3-butanediol; (B) O, acetaldehyde + acetal; Δ, diethyl ether.

measured in the presence of each inhibitor. Those that were measured are mentioned below.

The presence of ammonia had no effect on the yields of ethane, ethylene, or 2,3-butanediol. Ammonia reacts with acetaldehyde,¹³ so the influence of the former compound on the rate of formation of the latter could not be determined.

The addition of propylene to 860 torr of ethanol reduced *g*(acetaldehyde) from 3.2 to 1.8, whereas in 92 torr of ethanol the yield changed from 4.8 to 2.6 (Figure 4). Thus, as with the hydrogen yield, both the scavengable and unscavengable portions of the acetaldehyde yield increase with decreasing pressure.

In samples containing sulfur hexafluoride, most of the acetaldehyde was converted to acetal. The acid catalyst for the reaction was probably HF. The total acetaldehyde yield was considered to be the sum of those of acetaldehyde and acetal, and it increased from 3.2 to 6.1 as sulfur hexafluoride was added to 860 torr of ethanol (Figure 6).

In 860 torr of ethanol *g*(2,3-butanediol), originally 3.1, was decreased to <0.2 by propylene (Figure 4) and to 1.2 by sulfur hexafluoride (Figure 6).

The yield of diethyl ether, *g* = 0.15 in 860 torr of ethanol, was unaffected by propylene, but was increased to 2.4 by sulfur hexafluoride (Figure 6).

Sulfur hexafluoride also caused the appearance of 0.8 unit of diethoxymethane, which was probably formed by the acid-catalyzed reaction of formaldehyde with ethanol. This yield of diethoxymethane may be taken as the yield of formaldehyde in pure ethanol vapor, since the addition of sulfur hexafluoride did not alter the methane yield.

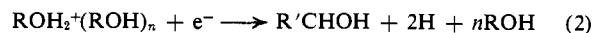
Discussion

Effect of Temperature. The effect on the product yields of changing the temperature in the range 60–200° is only slight (Figure 1). Anderson and Winter⁷ also studied the effect of temperature on the yields of hy-

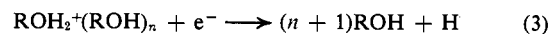
drogen and methane from ethanol vapor. They found that at an ethanol density of about 0.9 g/l, the hydrogen yield increased sharply between 100 and 150°, but that it was essentially independent of temperature from 80 to 100° and again from 150 to 200°. They suggested that the change in yield between 100 and 150° was associated primarily with changes in the ion-molecule equilibrium (1) and resultant differences in the charge neutralization products. For small values of *n*, two



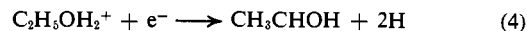
hydrogen atoms could be formed from a single neutrali-



zation step, whereas for large values of *n* only one hydrogen atom could be formed.⁷



We did not observe "two plateaus" in the hydrogen vs. temperature curve, as did Anderson and Winter,⁷ and do not agree with their interpretation of the temperature effect. By comparing the sizes of clusters of water and alcohol molecules about protons at different temperatures and pressures in the vapor phase,^{14,15} and in liquid acetonitrile at room temperature,¹⁶ one may see that in small clusters (e.g., *n* < 6, depending on conditions) alcohol molecules are held more readily than are water molecules, because of the larger polarizabilities of the former. In larger clusters alcohol molecules are less easily held to the cluster because of steric effects. We therefore estimate that in ethanol vapor at 1 atm of pressure, increasing the temperature from 100 to 150° would change the average value of *n* in reaction 1 from about 5 to 4. The solvation energy of H₃O⁺(H₂O)_{*n*} is about 103 kcal/mol for *n* = 5 and 93 kcal/mol for *n* = 4.¹⁵ The values would be roughly the same in ethanol. Since the reaction

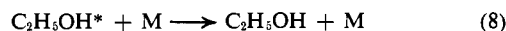
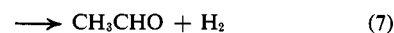


is only 30 kcal/mol exothermic,¹⁷ reaction 2 would be highly endothermic for *n* = 4 or 5.

The changes in product yields with temperature are due to differences in the activation energies of the reactions of the various intermediates, but it is not yet possible to specify which intermediates are involved.

Effect of Pressure. Anderson and Winter⁷ also observed that the hydrogen yield decreases with increasing pressure. They obtained a high-pressure plateau of *G*(H₂) = 10.6 at 175°, which is much higher than the value of about 6.2 that can be estimated from the present work. The discrepancy is probably mainly due to the different dosimeters used in the two studies.

The decrease in the hydrogen and acetaldehyde yields with increasing ethanol pressure (Figure 2) can be explained by the following reactions

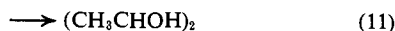
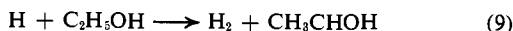


(14) P. Kebarle, R. N. Haynes, and G. J. Collins, *J. Am. Chem. Soc.*, **89**, 5753 (1967), Figure 4, 0.36 torr, 30°.

(15) P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *ibid.*, **89**, 6393 (1967), Figures 6 and 8.

(16) I. M. Kolthoff and M. K. Chantooni, Jr., *ibid.*, **90**, 3320 (1968).

(17) K. M. Bansal, Ph.D. Thesis, University of Alberta, 1968, p 177.



where M can be any molecule, but is ethanol in the present case. This is only a partial mechanism because it only contributes 4.2 of the 10.4 units of hydrogen formed at 150° (45 torr).

By applying the steady-state treatment to the above reactions one can obtain the following equations

$$\begin{aligned} \rho(\text{H}_2) &= \rho(\text{CH}_3\text{CHO}) \\ &= 1 + [k_8[\text{M}]/(k_6 + k_7)] \end{aligned} \quad (\text{ii})$$

where

$$\rho(\text{H}_2) = \frac{\Delta G(\text{H}_2)_{\text{max}}}{\Delta G(\text{H}_2)_{\text{max}} - \Delta G(\text{H}_2)}$$

$$\rho(\text{CH}_3\text{CHO}) = \frac{\Delta G(\text{CH}_3\text{CHO})_{\text{max}}}{\Delta G(\text{CH}_3\text{CHO})_{\text{max}} - \Delta G(\text{CH}_3\text{CHO})}$$

$\Delta G(\text{H}_2)_{\text{max}}$ and $\Delta G(\text{CH}_3\text{CHO})_{\text{max}}$ are the maximum decreases in the hydrogen and acetaldehyde yields that can be caused by increasing the pressure from zero to "infinity," $\Delta G(\text{H}_2) = G(\text{H}_2)_0 - G(\text{H}_2)$, $\Delta G(\text{CH}_3\text{CHO}) = G(\text{CH}_3\text{CHO})_0 - G(\text{CH}_3\text{CHO})$, and $G(\text{H}_2)_0 = 10.6$ and $G(\text{CH}_3\text{CHO})_0 = 5.0$ are the yields extrapolated to zero pressure. The yields at infinite pressure were obtained by extrapolating plots of the G values against (pressure)⁻¹ to (pressure)⁻¹ = 0; $G(\text{H}_2)_\infty = 6.2$ and $G(\text{CH}_3\text{CHO})_\infty = 2.0$.

A plot of $\rho(\text{H}_2)$ against ethanol pressure is shown in Figure 7A. The slope of the line corresponds to $k_8/(k_6 + k_7) = 53$ l./mol. This value of the rate constant ratio corresponds to $k_6 + k_7 = 5.5 \times 10^9$ sec⁻¹, assuming the collision efficiency of reaction 8 to be unity.

A plot of $\rho(\text{CH}_3\text{CHO})$ against ethanol pressure is given in Figure 7B. The line was drawn with the same slope as that in Figure 7A, as required by eq ii. The line fits the experimental points satisfactorily.

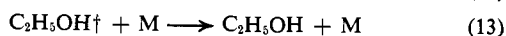
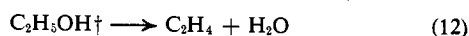
Steady-state treatment of reactions 5-11 also leads to eq iii. The value of $\Delta G(\text{H}_2)_{\text{max}}/\Delta G(\text{CH}_3\text{CHO})_{\text{max}}$ is

$$\frac{\Delta G(\text{H}_2)_{\text{max}}}{\Delta G(\text{CH}_3\text{CHO})_{\text{max}}} = \frac{k_6 + k_7}{k_7 + [k_6 k_{10}/(k_{10} + k_{11})]} \quad (\text{iii})$$

4.4/3.0 = 1.5. An upper limit for the value of k_{10}/k_{11} can be calculated from eq iii by assuming that $k_6 \gg k_7$; the value so obtained is $k_{10}/k_{11} = 2.0$. Results of Kato and Cvetanović¹⁸ indicate that $k_{10}/k_{11} = 0.7$ in the vapor phase at 25°. If this value also applies at 150°, then $k_6/k_7 = 1.3$.

The foregoing mechanism implies that $G(2,3\text{-butanediol})$ also increases with decreasing pressure.

The decrease in the yield of ethylene with increasing pressure (Figure 2) can be explained by a competition between reactions 12 and 13. Kinetic analysis of the



results by the same method as that described above gives $k_{13}/k_{12} = 82$ l./mol (see Figure 7C). This corresponds to a value of $k_{12} = 3.3 \times 10^9$ sec⁻¹, assuming the collision efficiency of reaction 13 to be unity, *i.e.*, $k_{13} = 2.9 \times 10^{11}$ l./mol sec).

(18) A. Kato and R. J. Cvetanović, *Can. J. Chem.*, **45**, 1845 (1967).

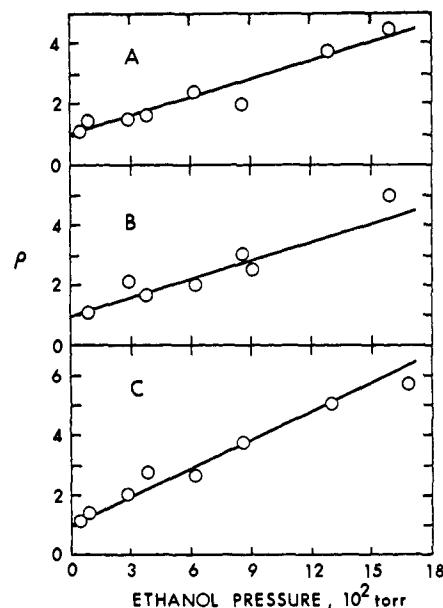
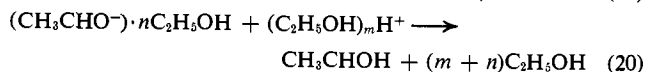
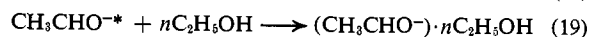
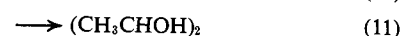
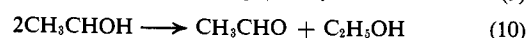
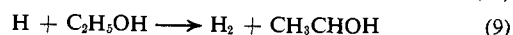
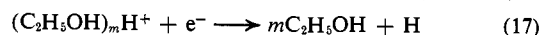
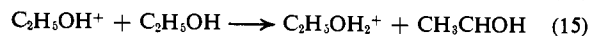
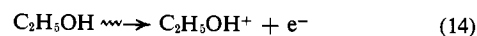


Figure 7. Kinetic plots of the effect of pressure on product yields: (A) hydrogen; (B) acetaldehyde; (C) ethylene $\rho = \Delta G_{\text{max}}/(\Delta G_{\text{max}} - \Delta G)$.

Effect of Radiation Dose. The yields of hydrogen and acetaldehyde decreased with increasing dose (Figure 3). No mechanism could be found that would explain a greater decrease in hydrogen than in acetaldehyde yield. Because of the difficulty of measuring the acetaldehyde in the low dose samples, the yields of this compound indicated in Figure 3 at the two lowest doses may be too small.

There is no information available about the rate of addition of hydrogen atoms to aldehydes, although the possibility that the reaction occurs has been suggested.^{19,20} In general, free radicals abstract from aldehydes much more readily than they add to them. For example, information given in ref 20 can be used to show that at 150° methyl radicals abstract from acetaldehyde 10⁴ times more readily than they add to the compound. It therefore seems unlikely that the dose effect in the present system can be explained in terms of hydrogen atom reactions.

The dose effect may be partly explained by the scavenging of electrons by acetaldehyde. The relevant portion of the mechanism is given below.



Reactions 16 and 19 each take place in several steps.

(19) B. A. Degraff and J. G. Calvert, *J. Am. Chem. Soc.*, **89**, 2247 (1967).

(20) M. T. H. Liu and K. J. Laidler, *Can. J. Chem.*, **46**, 479 (1968).

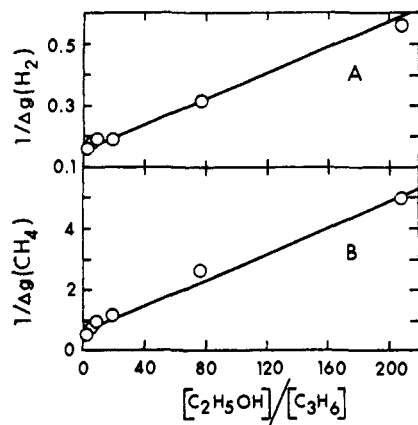


Figure 8. Kinetic plots for (A) hydrogen and (B) methane yields from the radiolysis of ethanol-propylene mixtures at 150° (ethanol pressure, 860 torr).

Charged molecular clusters, such as $(C_2H_5OH)_mH^+$, have been observed in several polar gases by mass spectrometry^{14, 15, 21-23} and by ion cyclotron resonance spectrometry.²⁴

At high doses, reaction 18 competes with reaction 17 for electrons. The value of $W_{C_2H_5OH}$ is 25.1 eV,²⁵ so $G(\text{ionization}) = 4.0$. Assuming a value of $k_{17} = 10^{14}$ l./mol sec,²⁶ the steady-state concentration of ions at a dose rate of 6×10^{19} eV/(l. hr) is 3×10^{-12} mol/l. At a dose of 7×10^{19} eV/g the decreases in the hydrogen and acetaldehyde yields are half of the maximum decreases caused by increasing the dose (Figure 3), so the rates of reactions 17 and 18 are roughly equal under these conditions. At 7×10^{19} eV/g the concentration of acetaldehyde was 5×10^{-8} mol/l., and it follows that $k_{18} \approx 10^8$ l./mol sec).

The values of electron attachment frequencies are similar for aldehydes and ketones of similar structure.²⁷ The electron attachment frequency in pure acetone vapor at 10 torr has been reported to be $400 \text{ torr}^{-1} \text{ sec}^{-1}$, which corresponds to a rate constant of 8×10^6 l./mol sec). The somewhat larger value of the rate constant for electron attachment to acetaldehyde ($\sim 10^8$ l./mol sec) in the present work is perhaps due to the stabilization of CH_3CHO^* by ethanol molecules (reaction 19). This view is supported by the fact that the electron attachment frequency of 2,4-pentanedione is nearly two orders of magnitude greater when methanol is the diluent vapor than when ethylene is the diluent.²⁷

The slight increases in the yields of methane and carbon monoxide with increasing dose (Figure 3) are probably due to the secondary decomposition of acetaldehyde.

Comparison of Product Yields Reported by Different Workers. The yields of products obtained from the radiolysis of ethanol vapor under different conditions

(21) P. K. Knewstubb and A. W. Tickner, *J. Chem. Phys.*, **38**, 464 (1963).

(22) M. S. B. Munson, *J. Am. Chem. Soc.*, **87**, 5313 (1965).

(23) L. W. Sieck, F. P. Abramson, and J. H. Futrell, *J. Chem. Phys.*, **45**, 2859 (1966).

(24) J. M. S. Henis, *J. Am. Chem. Soc.*, **90**, 844 (1968).

(25) P. Adler and H. K. Bothe, *Z. Naturforsch.*, **20a**, 1700 (1965).

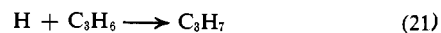
(26) G. R. Freeman, *Radiation Res. Rev.*, **1**, 1 (1968).

(27) L. Bouby, F. Fiquet-Fayard, and H. Abgrall, *Compt. Rend.*, **261**, 4059 (1965). The low attachment frequency reported for glyoxal in this paper is erroneous; see R. N. Compton and L. Bouby, *ibid.*, **264**, 1153 (1967).

in the present study are compared in Table I with those reported by other workers. Considering the effects of temperature, pressure, dose, and radiation quality, which were different from one study to the next, the product yields obtained by different workers only agree to within 10-20%. Agreement is even poorer than this for the yields of the glycols and acetylene. The main reasons for the discrepancies are probably that different dosimeters were used and that many of the analyses were difficult to perform accurately.

In our opinion, ethylene is the most reliable gas phase dosimeter currently in use. The value $G(H_2)_{C_2H_4} = 1.31$ is probably accurate to within 3%.¹⁰

Ethanol-Propylene Mixtures. 1. Ethanol Pressure 860 Torr. Hydrogen atoms add readily to propylene, giving isopropyl radicals.²⁸ The simplest interpretation of the decrease in hydrogen yield caused by the addition of propylene to ethanol (Figure 4) is that reaction 21 competes with (9). This competition for

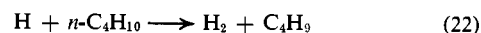


hydrogen atoms leads to the relationship

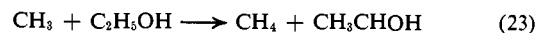
$$\frac{1}{\Delta g(H_2)} = \frac{1}{\Delta g(H_2)_{\max}} \left(1 + \frac{k_9[C_2H_5OH]}{k_{21}[C_3H_6]} \right) \quad (iv)$$

where $\Delta g(H_2)_{\max}$ is the maximum decrease in hydrogen yield caused by propylene.

A plot of $1/\Delta g(H_2)$ against $[C_2H_5OH]/[C_3H_6]$ is shown in Figure 8A. The slope and intercept of the line indicate that $\Delta g(H_2)_{\max} = 6.6$ and $k_9/k_{21} = 0.013$. The value of k_{21} at 150° is 1.0×10^9 l./mol sec,²⁹ so $k_9 = 1.3 \times 10^7$ l./mol sec) at this temperature. The value of k_9 may be compared with $k_{22} = 1.1 \times 10^7$ l./mol sec) at 150°.²⁹



The decrease in the methane yield (Figure 4) is attributed to the competition between reactions 23 and 24.



This competition leads to the relationship

$$\frac{1}{\Delta g(CH_4)} = \frac{1}{\Delta g(CH_4)_{\max}} \left(1 + \frac{k_{23}[C_2H_5OH]}{k_{24}[C_3H_6]} \right) \quad (v)$$

From the slope and intercept of the line in the plot of $1/\Delta g(CH_4)$ against $[C_2H_5OH]/[C_3H_6]$ in Figure 8B one obtains $\Delta g(CH_4)_{\max} = 1.5$ and $k_{23}/k_{24} = 0.029$. Using the value $k_{24} = 5.3 \times 10^4$ l./mol sec) at 150°, obtained in a system at about 3000 torr,³⁰ we get $k_{23} = 1.6 \times 10^3$ l./mol sec).

The various kinetic parameters are summarized in Table II.

The inhibition of the formation of acetaldehyde and 2,3-butanediol are also attributed to free-radical scavenging.

The portions of the products that were not scavengable by propylene have several possible modes of formation, for example, by decomposition of excited molecules or by reactions of ions or hot radicals. There

(28) R. J. Cvetanović, *Advan. Photochem.*, **1**, 115 (1963).

(29) A. F. Trotman-Dickenson, *Advan. Free Radical Chem.*, **1**, 1 (1965), Table 2.

(30) R. J. Cvetanović and R. S. Irwin, *J. Chem. Phys.*, **46**, 1694 (1967).

Table II. Summary of Kinetic Parameters^a in the Radiolysis of Ethanol-Propylene Mixtures at 150° and 8×10^{19} eV/g

Ethanol pressure (torr) at 150°	860	92
$G(\text{H}_2)$ scav ^b	6.7	7.8
$G(\text{H}_2)$ unscav	1.7	2.1
$G(\text{CH}_4)$ scav	1.5	1.8
$G(\text{CH}_4)$ unscav	1.6	1.3
$G(\text{CH}_3\text{CHO})$ scav ^b	1.3	2.2
$G(\text{CH}_3\text{CHO})$ unscav	1.8	2.6
$G((\text{CH}_3\text{CHOH})_2)$ scav	3.1	
$G((\text{CH}_3\text{CHOH})_2)$ unscav	0.0	
k_9/k_{21}	0.013	0.012
$k_9, 10^7 \text{ l.}/(\text{mol sec})$	1.3	1.2
k_{23}/k_{24}	0.029	0.072
$k_{23}, 10^3 \text{ l.}/(\text{mol sec})$	1.6	

^a scav = scavengeable; unscav = unscavengeable. ^b The scavengeable yields of hydrogen and acetaldehyde at "zero" dose would be somewhat larger than those reported here.

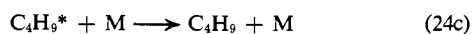
is not enough information available to make a choice between them.

Consideration of possible reactions between propylene and various charged species in the system led to the conclusion that propylene does not interfere to an appreciable extent with the ionic reactions.³¹

2. Ethanol Pressure 92 Torr. The same kinetic treatment as above was given to the results obtained at the lower ethanol pressure. The values of the parameters derived from the kinetic analysis are listed in Table II.

3. Effect of Pressure on the Values of k_9/k_{21} and k_{23}/k_{24} . The value of k_{23}/k_{24} was larger at 92 torr than at 860 torr, whereas that of k_9/k_{21} was essentially independent of pressure (Table II). The rate constants of the metathetical reactions 9 and 23 would be independent of pressure. Thus the rate constant for the addition reaction 24 increases with increasing pressure and that of the addition reaction 9 is independent of pressure over the range studied.

The addition reaction 24 should be written as a combination of reactions (24a-c).



where M is a third body. By writing

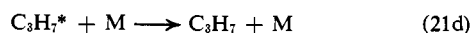
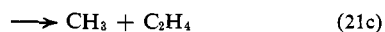
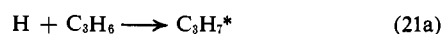
$$k_{24}[\text{CH}_3][\text{C}_3\text{H}_6] = k_{24a}[\text{CH}_3][\text{C}_3\text{H}_6] - k_{24b}[\text{C}_4\text{H}_9^*] \quad (\text{vi})$$

and applying the steady-state treatment to the C_4H_9^* concentration, it can be shown that

$$k_{24} = k_{24a} \left(\frac{k_{24c}[\text{M}]}{k_{24b} + k_{24c}[\text{M}]} \right) \quad (\text{vii})$$

Equation vii explains the pressure dependence of k_{24} .

Similarly the net reaction 21 can be represented in the following manner.



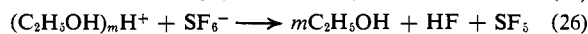
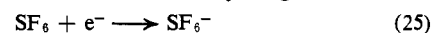
Therefore

$$k_{21} = k_{21a} \left(\frac{k_{21c} + k_{21d}[\text{M}]}{k_{21b} + k_{21c} + k_{21d}[\text{M}]} \right) \quad (\text{viii})$$

(31) Reference 17, pp 187-188.

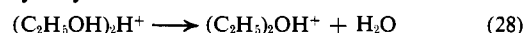
Since k_{21} was independent of pressure between 92 and 860 torr, reactions 21c + 21d occur to the virtual exclusion of (21b) under these conditions.

Ethanol-Sulfur Hexafluoride Mixtures. Sulfur hexafluoride has a very large capture cross section for thermal electrons,³² so it interferes with the electron neutralization reactions. Replacement of reactions 17 and 9-11 by 25-27 causes the hydrogen and bu-



tanediol yields to decrease and that of acetaldehyde to increase (Figure 6). The magnitudes of the yield changes shown in Figure 6, adjusted for the fact that the measurements were made at a dose of 8×10^{19} eV/g rather than at "zero" dose, are consistent with reaction 25 occurring to the extent of four G units ($W_{\text{C}_2\text{H}_5\text{OH}} = 25.1 \text{ eV}^{25}$).

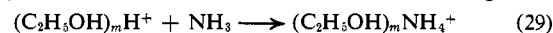
The small yield of diethyl ether in pure ethanol may be formed by way of the reaction



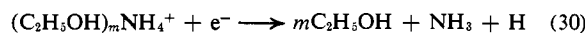
Reaction 28 and its equivalent in methanol have been observed by mass spectrometry²³ and by ion cyclotron resonance spectrometry.²⁴ The addition of sulfur hexafluoride to the radiolysis system increased g - (diethyl ether) from 0.15 to about 2.0 (Figure 6). The increase of yield may be due to the reaction of sulfur tetrafluoride with ethanol. Sulfur tetrafluoride is a proposed product (reaction 27) and is known to react with alcohols in such a way that ethers are formed.³³

Ethanol-Propylene-Sulfur Hexafluoride Mixture. At the ethanol pressure (860 torr) and dose (8×10^{19} eV/g) used, $\Delta g(\text{H}_2)_{\text{max}}$ equals 6.7 for propylene addition and 3.0 for sulfur hexafluoride addition. The only hydrogen precursor scavenged by propylene in this system is hydrogen atoms, and 5.2 mol % propylene causes $\Delta g(\text{H}_2) = 4.8$ (Figure 4). Sulfur hexafluoride scavenges only electrons and 3.2 mol % of the scavenger causes $\Delta g(\text{H}_2) = 3.0$. The addition of 5.2 mol % propylene and 3.2 mol % sulfur hexafluoride to the same ethanol sample caused $\Delta g(\text{H}_2) = 5.7$. This is 0.9 unit more than that caused by the propylene alone and is the amount expected, $(6.7 - 4.8)3.0/6.7 = 0.9$, if ion-electron neutralization produces hydrogen atoms rather than molecular hydrogen directly. Thus it may be concluded that the direct formation of molecular hydrogen from ion-electron neutralization in ethanol vapor at 150° is negligible.

Ethanol-Ammonia Mixtures. Ammonia had no effect on the rates of formation of the products. The proton affinities of ammonia and ethanol are 209 ± 7 and 193 ± 8 kcal/mol,²⁶ respectively, so reaction 29 probably occurs. Whether the value of m changes as



a result of reaction 29 depends on the structures of the $(\text{C}_2\text{H}_5\text{OH})_m\text{H}^+$ and $(\text{C}_2\text{H}_5\text{OH})_m\text{NH}_4^+$ clusters. The neutralization of either cluster by an electron results in the formation of a hydrogen atom, so the ultimate products of the reactions are the same.



(32) A. N. Prasad and J. D. Craggs in "Atomic and Molecular Processes," D. R. Bates, Ed., Academic Press, New York, N. Y., 1962, Chapter 6.

(33) H. L. Roberts, *Quart. Rev.* (London), 15, 30 (1961).